REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	08 Jun 95	Annual Technical: 15 Jul 93 –08Jun95

4. TITLE AND SUBTITLE

Novel Sol-Gel Composite Second Harmonic Generator and Electrooptic Modulator

5. FUNDING NUMBERS

F49620-92-C-0046

1602-01

63218C

6. AUTHOR(S)

Ryszard Burzynski and Martin Casstevens

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Laser Photonics Technology, Inc.
1576 Sweet Home Rd
Amherst, NY 14228

8. PERFORMING ORGANIZATION REPORT NUMBER

AFOSR-IR 95 - 0 4 4 9

LPTP2AATR2

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
110 Duncan Ave, Suite B115
Bolling AFB, DC 20332-0001

Dr Charles Y-C Lee

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This document is submitted as the second annual technical report for contract No. F49620-92-C0046 and presents LPT's work on the preparation of second-order NLO composite materials. The approach employed in this work is to use NLO ormosils and sol-gel preparation techniques to produce homogeneous composite materials for fabrication of optical wave guides. The use of electric field poling technique introduces the required second-order nonlinearity which can be utilized to generate a second harmonic frequency or for high frequency light modulation. The materials that are developed exhibit sufficient nonlinearity for devices and low optical losses. The report contains a full description of the synthetic approaches, characterization and processing of the materials, the thermal and temporal stabilities of NLO responses and measurements of waveguide propagation losses.

19950626 027

DTIC QUALITY INSPECTED 3

14. SUBJECT TERMS

sol-gel, ormosil, composite, chromophore, nonlinear optics, electrooptic

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	U

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

Table of Contents

Distribution /

Availability Codes

Dist	Avail and / or Special
A-1	

A. Project Summary

"Novel Sol-Gel Composite Second Harmonic Generator and Electrooptic Modulator"
Contract No. F49620-92-C-0046

Second Year Annual Report
(15 July 1993-14 July 1994)

P.I. - Dr. Ryszard Burzynski

Abstract

The results of the first two years of work involving sol-gel composite second-order nonlinear optical materials (funded under SBIR contract No. F49620-90-C-0046) are presented in this document. The general goal throughout this stage of the program was to utilize the proposed sol-gel composites to: (i) produce optical quality films; (ii) induce non-centrosymmetric alignment of the chromophores with large hyperpolarizabilities (β) by a modified electric field poling technique; (iii) optimize poling parameters by using *in-situ* poling method; and (iv) test the temporal stability of the processed composites by means of second harmonic generation and electrooptic modulation experiments.

The present work involves a sol-gel processing technique, originally developed in the Phase I feasibility studies by the staff of Laser Photonics Technology, Inc., to yield final materials in which both the organic and inorganic components perform important roles. Sol-gel processing is the procedure employed in the R & D effort because of its proven reputation for producing homogeneous materials (liquid mixing), the relatively low temperatures which are required to produce composite glasses, and because of the potential of these materials to preserve second order chromophores in a non-centrosymmetric arrangement induced by the external electric field. This conjecture has been confirmed by experimental data which show that the second order activities of fabricated composites exhibit temporal stability at room temperature. Additional experiments assessing the temporal stability of second order responses at elevated temperatures have been initiated and, predictably, indicate that the relaxation processes are accelerated under these conditions. The report documents LPT's continued efforts to develop new, ORMOSIL based composites to address the temporal and thermal stability of the nonlinear optical response(s). The manifestation of these systems in a wave guide geometry have been examined at several wavelengths and indicate that the ORMOSIL composite films exhibit optical losses of the order of 3 dB/cm. Further improvements in optical quality are expected with optimized processing and poling conditions.

SUMMARY OF GOALS AND OBJECTIVES

The technical work of the Phase II development program is comprised of two major tasks:

- Synthesis of sol-gel glass composite(s) for optical wave guide fabrication; and
- Synthesis of sol-gel glass composite(s) for high frequency electrooptic light modulators.

The majority of the effort on this contract was focused on deriving the most appropriate multifunctional photonics materials for use in specific optical devices such as waveguide second harmonic generators or electrooptic light modulators. The staff of LPT aimed to optimize sol-gel processing conditions to achieve exceptional optical quality of the resulting composite films as well as demonstrating temporally and thermally stable alignment of the second order nonlinear optical chromophores. The accomplishment of these goals involved chemical syntheses of the chromophores and extensive characterization of their compatibility with sol-gel processing, a thorough evaluation of the Nonlinear Optical (NLO) properties, and the thermal and temporal stabilities. This effort also encompassed (1) the syntheses of chemically modified silicon alkoxides through the covalent attachment of an NLO chromophore, and (2) systematic optimization of ormosil processing conditions resulting in optical waveguide quality films.

ANNUAL RESEARCH AND DEVELOPMENT REPORT

The primary objective of the proposed research and development work in the second year of the Phase II effort was to produce optical quality sol-gel composites exhibiting a high second order optical figure of merit by utilizing the unique material processing technique developed under the Phase I feasibility studies and previous work accomplished in the first year. The second objective was to optimize the processing conditions of the sol-gel composites in an effort to produce a large and temporally stable second order nonlinear response. Previous efforts to dope sol-gel matrices met with some success. The chief shortcoming of these materials were that (1) they had a tendency to phase segregate and (2) the retention of chromophore orientation did not exceed the performance of several other systems. The second year work involved developing ormosil systems which are expected to address the deficiencies of materials developed in earlier stages of the work. These efforts included:

(1)   syntheses of Ormosils containing NLO chromophores with large β values;

(2)   a determination of optimal sol-gel processing conditions for NLO ormosils;

(3)   fabrication of the composite materials containing NLO Ormosils and sol-gel silica which yield materials of acceptable (low loss) optical quality;

(4)   the use of a modified *in-situ* electric field poling technique to establish poling conditions such as temperature, time and electric field strength;

(4)   measurements of second order responses over long periods of time;

(5)   measurements of the thermal stability of the the non-centrosymmetric alignment of chromophore molecules in sol-gel composite matrices.

LPT's efforts conducted during this period concluded with the following accomplishments:

►   syntheses of three second order ormosils with covalently attached large β value chromophores: (1). 4-[N,N-(2,2'-dihydroxyethyl)amino]-4'- nitrostilbene (DHD), (2) N-(4-nitrophenyl)-(L)-prolinol (NPP) and (3) 4-[2,2'-dihydroxyethyl)amino]-4'-(6-hydroxyhexylsulfinyl)stilbene (THS);

►   successful preparation of sol-gel oxide/$\chi^{(2)}$ chromophore ormosil composites consisting of up to 80 wt% of the $\chi^{(2)}$ Ormosil and fabrication of films exhibiting excellent optical quality;

►   preparation of sol-gel processed pure $\chi^{(2)}$ Ormosil films of optical quality;

►   optimization of electric field poling parameters by the use of an *in-situ* poling technique to achieve effective and stable non-centrosymmetric arrangement of the chromophores (the average $\chi^{(2)}$ value for a composite containing DHD Ormosil (DHDO) was measured to be 3.5×10^{-7} esu);

►   fabrication of an improved poling apparatus containing a set of electrodes which enhance the poling process and prevent surface damage;

►   temporal and thermal stability measurements of the chromophores and composites;

►   electrooptic measurements on selected samples;

►   evaluation of propagation losses at different wavelengths for waveguides made of DHDO.

The performed work clearly shows that sol-gel silica and sol-gel silica/ormosil matrices containing second-order chromophores can be used to form high optical quality films of waveguide dimensions and that electric field poling scheme can be used to obtain stable noncentrosymmetric arrangement of the chromophores.

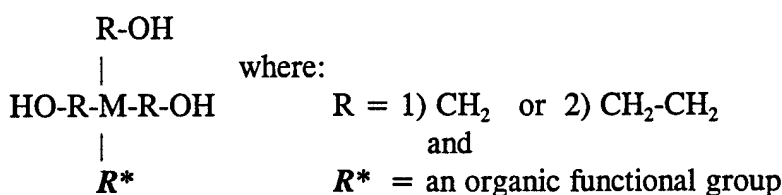## B. Sol-Gel and Ormosil Composite Materials for Second Order Nonlinear Optical Applications

B-1 INTRODUCTION

The work reported in this document describes in detail the efforts aimed at designing sol-gel processed NLO materials wich have the potential of being utilized as active elements in optical circuitry. The emphasis throughout this work has been placed on chemistry and material processing of ormosils which ultimately determine the performance and utility of the composite materials. A rationale of the selected approach is presented in the following sections. An introduction to a fundamentals of sol-gel processing and application of NLO materials in photonics in general has been given previously; the reader is referred to the first years annual report for this information.

Important applications for second-order NLO materials are in electrooptic light modulation and second harmonic generation. The performance of such devices are determined by the NLO materials, ie., their nonlinearity, optical transparency, thermal stability, the driving voltage (or the modulation voltage) for a specific modulation depth, the modulation bandwidth, the magnitude of the optical losses (insertion, scattering and absorption) and the manufacturing costs (or ease of fabrication). Each of these considerations stems directly from the properties of the wave guide material itself. Therefore, an electrooptic material must first be selected that has a high electrooptic coefficient and low optical losses.

The growing interest in organic and polymeric materials and their applications in integrated optical devices have resulted in a number of promising materials which have been demonstrated to be suitable for integrated electrooptic modulators. Organic molecular materials are believed to exhibit the largest nonresonant optical nonlinearities. Several organic crystals have been shown to possess electrooptic coefficients as high as 600 pm/V with dielectric constants as low as 3.[1] In amorphous materials, molecules with high hyperpolarizabilities are either doped into a host polymeric matrix or attached to a polymer as a side chain or a segment of the main chain, and an electric field poling process aligns the dipolar molecules in the direction of the field and breaks the center of symmetry. After poling, the material is noncentrosymmetric and shows an electrooptic response. High frequency modulation of polymer based optoelectronic systems have been demonstrated at 20 GHz[2] and 40 GHz[3] in traveling wave devices. In addition, the underlying optoelectronic response of a polymer film has been demonstrated up to 460 GHz.[4] The electronic nature of the electrooptic response in organic materials suggests that they will find an increasing number of applications based upon the desire to operate at higher frequencies.

Conventional sol-gel processed alkoxides lead to inorganic materials that are extremely homogeneous and atomically pure. This technology has found many applications. Ormosils are related to alkoxides, but retain an organic functionality after processing. These materials are also very homogeneous, but exhibit properties that reflect their inorganic - organic composition. They may be used alone or mixed with either polymers and or conventional alkoxides.Chemical structure of ormosil is shown below and further description in the next section.

$$
\begin{array}{ll}
\text{R-OH} & \\
\quad | & \text{where:} \\
\text{HO-R-M-R-OH} & \quad R = 1)\ CH_2 \quad \text{or} \quad 2)\ CH_2\text{-}CH_2 \\
\quad | & \qquad\qquad \text{and} \\
\quad R^* & \quad R^* = \text{an organic functional group}
\end{array}
$$

B.2. ORMOSILS

(1) Homogeneity and optical quality

Since the sol-gel process is carried out in solution, a homogeneous mixture of miscible precursors can be readily achieved. Doped sol-gel systems result in the uniform distribution of various dopants but are susceptible to phase segregation over time and with thermal cycling. Ormosils, on the other hand, are molecules essentially free of dopants. The NLO species are bound to the matrix covalently and, therefore, ormosils can be viewed as single phase materials.

(2) Multicomponent and multifunctionality

Sol-gel materials can be prepared at low temperatures; it is thus possible to prepare numerous composite structures by incorporating inorganic and organic species without inducing thermal decomposition of the latter components. For example, 2-methyl-4-nitroaniline (MNA), *para*-nitroaniline (PNA), p-(diethyl amino) nitrostyrene (DEANST), and many other second order chromophores have been successfully doped by LPT staff into SiO_2/TiO_2/organic polymer matrices using the sol-gel process. The simplicity of this approach is extremely attractive and can be accomplished without custom synthesis. The same flexibility can be accomplished with ormosil approach, but it requires the design of ormosils having the appropriate chemical properties and reactivities. Thin films of these materials have been shown to be of optical wave guide quality and have been further used as nonlinear optical materials. The incorporation of organic photochromic, fluorescent or absorbing species within these type of matrices can be similarly performed yielding materials useful in such applications as sensors, optical memory media, etc.

(3) Electric field poling during densification

The electric field poling procedure used for polymers can be modified for use with sol-gel materials. By applying the electric field prior to the heat treatment, molecules can be oriented effectively because of their high orientational mobility within the non-densified glassy matrix. Subsequent heat treatment is designed to "fix" the molecules in a preferable orientation.

(4) Refractive index variation for optical wave-guiding

For optical wave guide applications, judicious control of the refractive index of the film is essential. This can be achieved by changing the relative composition of SiO_2, TiO_2, or other high index inorganic oxides as well as the composition of other components. Furthermore, because of the presence of an organic component, films of waveguiding dimensions (about 1 μm) can be formed by a single coating without the problem of cracking which is typical of "thick" sol-gel films.

(5) Device fabrication

The relative ease with which one can control the processing parameters renders this technique suitable for the fabrication of thin films, optical wave guides (both channel and planar)and even optical fibers; these forms are amenable to common device fabrication techniques.

In the following section we present a brief introduction to a chemically modified organometallic precursors to ceramic materials, commonly called ormosils.

C.   NLO Chromophores and NLO Sol-Gel Composites

The following sections describe the work accomplished over the initial period of the Phase II research effort. In this report, we present the experimental results on the second-order nonlinear optical properties of several material composites prepared by the sol-gel process. Second-Harmonic Generation (SHG) and electrooptic modulation are the principal means by which these samples are characterized. The materials have been tested for a relatively long period of time in order to assess the temporal stability of the poled structures at room temperature. The stability of the second-order optical response of the samples exposed to elevated temperatures for several hours has also been evaluated. Finally, we outline the work currently in progress, and the planned work for the remaining term of the contract.

C.1.   SYNTHESIS AND COMPOSITE PREPARATION

C.1.1. Preparation of DHD

Pyridine (32 mL, 0.4 mol) was added to a solution of 14.5 g (80 mmol) N-phenyldiethanolamine (A) in 100 mL dichloromethane followed by 30 mL (0.32 mol) acetic anhydride and the solution was stirred for 1 h. The reaction was quenched with water and was worked up using a copper sulfate solution to remove excess pyridine, this was followed by the addition of water and a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to yield 20.8 g (98 %) of acetylated A.

Phosphorus oxychloride (3 mL, 31.5 mmol) was dropwise added to 10 mL (126 mmol) of dry dimethylformamide (DMF) at 0-5 °C under a nitrogen atmosphere. N-Phenyldiacetoxy-ethylamine (8.36 g, 31.5 mmol) was added dropwise to the above reaction mixture resulting in
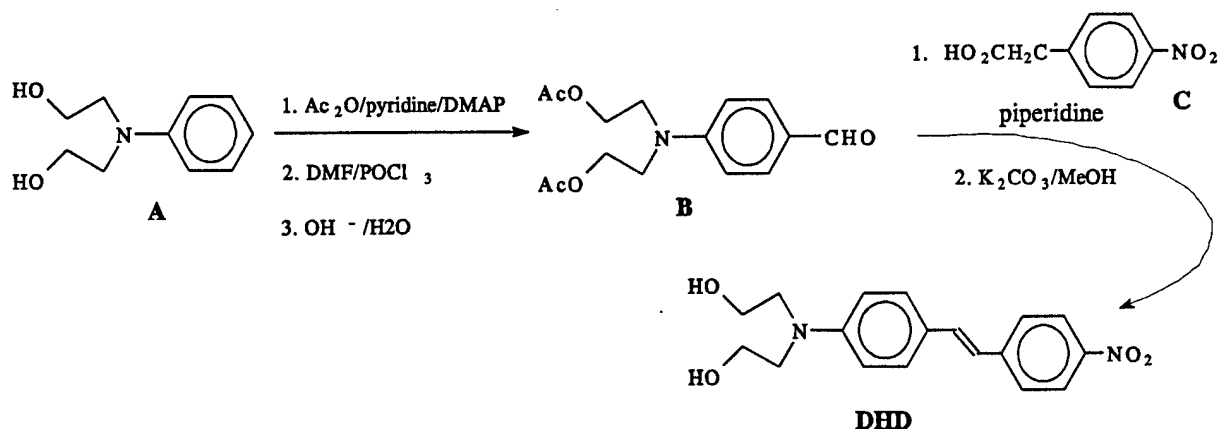

Figure 1 Synthesis of NLO chromophore DHD.

the appearance of a thick yellow precipitate. The reaction flask was subsequently heated at 100 °C for 2 h. whereupon the precipitate dissolved and the color of the solution turned brownish. The mixture was then cooled to room temperature and was poured in 200 mL of a ice water mixture with vigorous stirring. The solution was neutralized carefully using saturated sodium hydroxide. The precipitate formed was filtered, washed with water and air dried. The solid was dissolved in a minimum amount of methylene chloride and passed through a short silica gel column. The slight yellowish solution obtained after this filtration type chromatography was evaporated to yield 8.86 g (96%) of B.

The next step of stilbene formation was performed according to work published by DeMartino (R.D. DeMartino U.S. Patent 1988, 4,757,130). Piperidine (2.6 mL, 2.21 g, 26 mmol) was dropwise added to 4.71 g (26 mmol) 4-nitrophenylacetic acid (C) under nitrogen at room temperature. 4-(N,N-(2,2'-diacetoxyethyl)amino)-benzaldehyde (B) (5.86 g, 20 mmol) was added to this mixture and stirred well. The mixture was then heated at 100 °C for 1 h and at 130 °C for 3 h. It was then cooled to room temperature and 50 mL of methanol was added followed by 5.52 g potassium carbonate. After stirring for 10 mins., the mixture was filtered and the precipitate was washed with water, air-dried, and recrystallized from toluene (~0.5 L). The yield for the shiny chocolate brown colored flakes of DHD was 2.1 g (32%). M.P. 181-181.5 °C. R_f = 0.11 in 1:1 EtOAc-hexane. ^{1}H-NMR (300 MHz, DMSO-d_6) 8.13, 7.71 (ABq, 4H, J = 8.79 Hz), 7.42, 6.69 (ABq, 4H, J = 8.79 Hz), 7.38, 7.05 (ABq, 4H, J = 16 Hz), 4.78 (t, 1H), 3.51 (t, 4H), 3.45 (t, 4H).

C.1.2. Synthesis of THS

Chemistry of the THS preparation is schematically shown in Figure 2. A detailed description of each step is presented below.

6-Hydroxyhexyl-*p*-tolyl sulfide (2): To 500 mL ethyl alcohol under nitrogen at room temperature was slowly dissolved 13 g (0.562 mol) of sodium globules. The solution was brought to 0-5 °C and 63.5 g (0.511 mol) thiocresol was added followed by 80 g (0.562 mol) of 6-chloro-1-hexanol (96%). The temperature of the mixture was raised and refluxed for 10 h. After cooling, the reaction mixture was filtered and the solvent was evaporated off. After filtering through a short silica gel column using methylene chloride as a solvent, the crude white material was recrystallized from hexane to yield 109 g. (95%) of 2. M.P. 45 °C.

6-Acetoxyhexyl-p-tolylsulfide (3): In a 1 liter round bottom flask, 77.5 g (0.346 mol) of 2 was dissolved in 500 mL of dry methylene chloride and 70.6 g (65 mL, 0.692 mol) acetic anhydride was added followed by 55 g (56 mL, 0.692 mol) of pyridine. A catalytic amount (4.2 g, 34.6 mmol) of N,N-dimethylaminopyridine (DMAP) was added to the clear solution and it was stirred for 1 h. The reaction was quenched with the addition of water and the methylene chloride layer was washed with 10 % aqueous solution of cupric sulfate until all the pyridine was removed (checked by tlc); the was followed by the addition of water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium

sulfate and evaporated to give a clear oil.

6-Acetoxyhexyl-p-tolylsulfinate (4): In a one liter round bottom flask, 92 g (0.346 mol) of the sulfide **3** was dissolved in 350 mL glacial acetic acid and heated to reflux. Hydrogen peroxide (80 mL, 0.692 mol) was added dropwise from thetop of the reflux condenser at the rate to keep the boiling solution under control. After the total addition of hydrogen peroxide, the solution was refluxed for 2 h followed by distilling off the acetic acid. The clear liquid was washed with water and saturated sodium chloride solution and was dried over anhydrous magnesium sulfate to yield 100 g (97 %) of **4**. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.76, 7.34 (AB$_q$, J = 8 Hz, 4H), 4.00 (t, 2H), 3.05 (t, 2H), 2.45 (s, 3H), 2.02 (s, 3H), 1.69 (m, 2H), 1.56 (m, 2H), 1.34 (m, 4H) ppm.

6-Acetoxyhexylsulfinyl benzyl bromide (5): In a one liter round bottom flask equipped with a straight condenser, 100 g (0.336 mol) of sulfinate **4** was dissolved in 300 mL of dry carbon tetrachloride. The solution was brought to reflux and a mixture of 59.7g (0.336 mol) N-bromosuccinimide and 8.13 g (33.6 mmol) of benzoyl peroxide was added portionwise over a time period of 1 h. The progress of the reaction could be followed by the formation of succinimide which is less dense than the solvent. After 10 mins. of refluxing, the mixture was cooled rapidly to 0-5 °C and was filtered to remove succinimide. The filtrate was left in the refrigerator for 2 days with occasional scratching on the side of the flask. The crystals formed were filtered and dried under vacuum to yield 88.17g (70 %) of pure white **5**. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.88, 7.58 (ABq, J = 8 Hz, 4H), 4.505 (s, 2H), 4.01 (t, 2H), 3.09 (t, 2H), 2.02 (s, 3H), 1.75 (m, 2H), 1.60 (m, 2H), 1.37 (m, 4H) ppm.

6-Acetoxyhexylsulfinyl benzyl phosphonate (6): To 20.73 g (55 mmol) of melted bromide **5**, at 100 °C, under nitrogen, 13.7 g (14.13 mL, 82.5 mmol) of triethyl phosphite was added dropwise over 20 minutes. The solution was heated to 120 °C and kept for 2 hours. Excess triethyl phosphite was distilled off and the thick colorless liquid was used for the next step without further purification.

N-Phenyldiacetoxyethylamine (8): In a one liter round bottom flask, 45.25 g (0.25 mol) of **7** was dissolved in 500 mL of dry methylene chloride; 102 g (92 mL, 1.0 mol) of acetic anhydride was added to it followed by 49 g (50 mL, 0.625 mol) of pyridine. A catalytic amount (3.0 g, 25 mmol) of N,N-dimethylaminopyridine (DMAP) was added to the clear solution and stirred for 1 h. The reaction was quenched with the addition of water and the methylene chloride layer was washed with 10 % aqueous solution of cupric sulfate, until all the pyridine was removed (checked by tlc), followed by water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and was evaporated to give 63.6 g (96 %) of a clear oil (**8**).
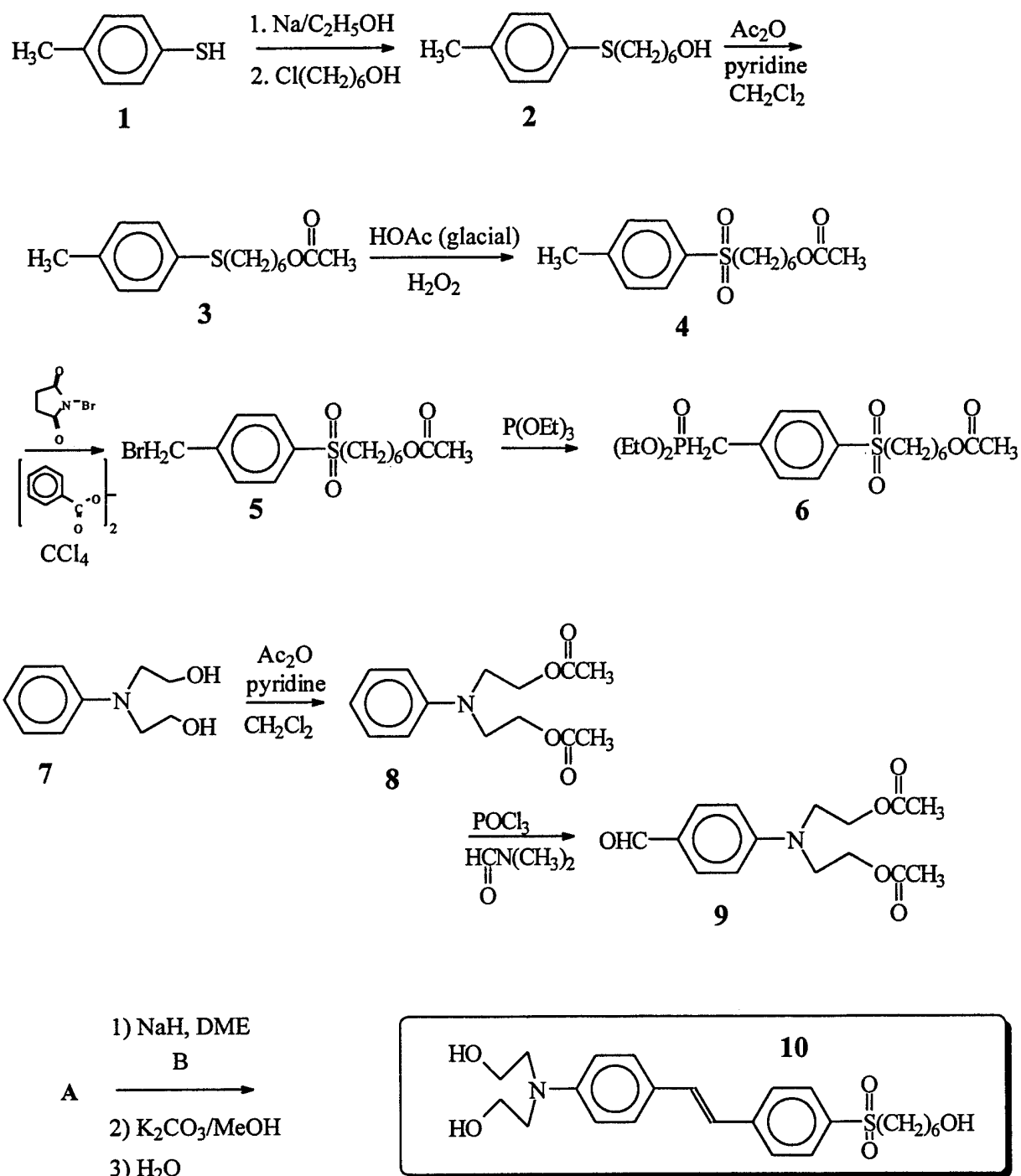
12

Figure 2 Preparation of THS chromophore (**10**)

4-(2,2'-Diacetoxyethylamino)benzaldehyde (9): To 75 mL DMF at 5 °C under nitrogen, 23 mL of phosphorus oxychloride was added dropwise. To this light brown colored solution, 63.3 g (0.239 mol) of the acetate **8** was added. Towards the end of the addition, the cooling bath was removed due to difficulty in stirring the thick yellow precipitate. This slurry was then heated for 1.5 h, cooled to room temperature and poured into 400 mL ice cold water. A cooled solution of 40 g (1 mol) sodium hydroxide in a minimum amount of water was dropwise added to neutralize the brown solution. The solution was filtered and washed with water. The crude material was dried under vacuum, dissolved in methylene chloride and filtered through a silica gel column with a 1:2 ethyl acetate-hexane mixture. Total yield after evaporation was 54.5 g (78 %). M.P. 54-6 °C. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 9.72 (s, 1H), 7.71, 6.78 (AB$_q$, J = 8.5, 4H) 4.26 (t, 4H), 3.7 (t, 4H), 2.01 (s, 6H) ppm.

4-Diethanolamino-4'-(6-hydroxyhexylsulfinyl)stilbene (10): To 1.2 g (30 mmol) of sodium hydride (60 % dispersion in mineral oil) (washed with 3 x 5 mL dimethylethylene glycol [DME]), a solution of 13.0 g (30 mmol) of phosphonate **6** in dry DME was added followed by 8.79 g (30 mmol) aldehyde **9**. The mixture was refluxed for 2 days. The reaction mixture was cooled and quenched with water. The excess solvent was removed under vacuum and was filtered through silica gel using ethyl acetate as solvent. The solvent was evaporated and the sticky yellow material was dissloved in 500 mL methanol followed by addition of 12.4 g (90 mmol) of potassium carbonate. The mixture was stirred for 2 h. and excess potassium carbonate was filtered off. Two thirds of the solvent was evaporated under vacuum and the rest of the thick solution was poured into an ice water mixture. The yellow precipitate was collected by filtration and recrystallized from chloroform to yield 1.8 g (13 %) of **10**. M.P. 120 °C. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.73 (q, 4H), 7.41, 6.67 (AB$_q$, J = 8.5, 4H), 7.30, 7.00 (AB$_q$, J = 8.5, 4H), 4.76 (t, 2-OH), 4.30 (t, 1-OH), 3.50 (m, 4H), 3.42 (m, 4H), 3.25 (m, 4H), 1.50 (m, 2H), 1.25 (m, 6H) ppm.

C.1.3. Preparation and General Processing of DHD ORMOSIL (DHDO)

A. *Preparation of DHDO.*

In a 50 mL flask, a mixture of 1.31 g (4 mmol) DHD, 2.96 g (12 mmol, 3 equiv.) 3-(triethoxysilyl)propyl isocyanate, 2 mL chlorobenzene, and 6 drops of hexamethylphosphoric triamide (HMPA) was heated for 24 hours at 110 °C. Chlorobenzene was distilled off under vacuum and the remaining dark red colored semi-solid was diluted with 3 mL freshly dried isopropanol and left sealed under nitrogen until further use.

B. *General Processing.*

(i) Hydrolysis: A mixture of 450 mg 88% formic acid (containing 54 mg of water, 3 equivalent of each triethoxysilane group) and 600 mg freshly dried butanol was added to 606 mg (1 mmol triethoxysilane content) of the ORMOSIL solution. The solution was sonicated for 10 mins. at room temperature and then heated at 60 °C for 10 mins.

(ii) Film Formation: The solution was always cooled to room temperature, filtered through 0.2 μm filter and spincoated at 600 rpm on ITO coated glassplates. The film was dried at 100 ^{0}C under vacuum for 2.5 h.
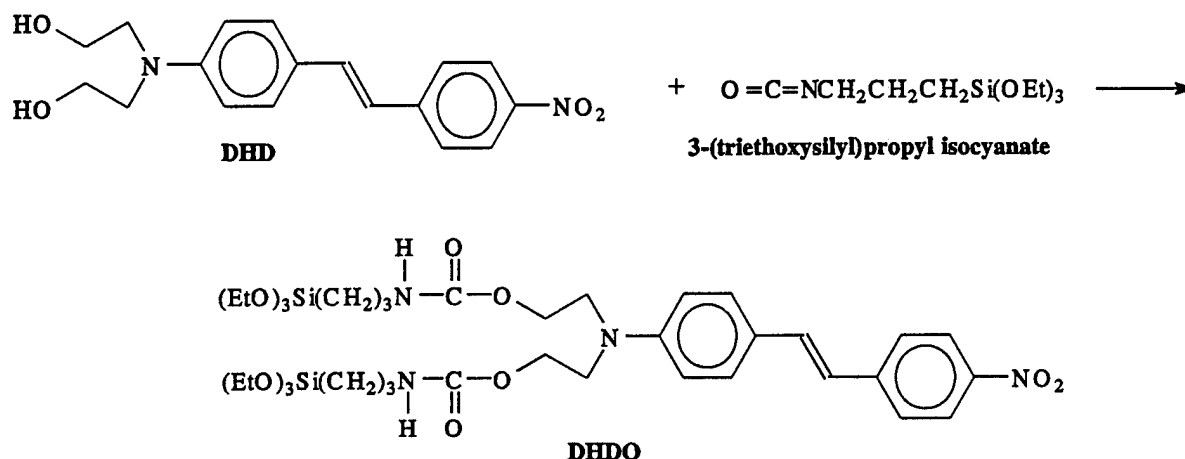

Figure 3 Chemical route to DHDO

C. *General Fabrication of Composite Materials with Sol-Gel Silica.*

A mixture of 450 mg 88% formic acid (containing 54 mg of water, i.e., 3 equivalent for each triethoxysilane group) and 600 mg freshly dried butanol was added to 606 mg (1 mmol Si content) of the DHDO solution. The solution was sonicated for 10 mins. at room temperature, and then heated at 60 ^{0}C for 10 mins. It was cooled to room temperature, and mixed with 184 mg (0.5 mmol Si) of sol-gel silica (TEOS prehydrolyzed either with 1.5 or 4 mole equivalents of water using a mild catalyst). The resulting clear solution was stirred for 5 mins. at room temperature, filtered through a 0.2 μm filter and spincoated at 600 rpm on ITO coated glass plates. The film was dried at 100 ^{0}C under vacuum for 2.5 h.

D. *Application of Protective Coatings.*

Two protective coatings were used in an effort to decrease high temperature conductivity (Accuglass 311) and damage to the sample surface caused by high energy ions produced in corona discharge (polymer resins). In the first case the coating was applied to the ITO surface; in the latter, polymer films were applied over the NLO films.

The coatings were applied as follows: Slides with ITO electrodes were cleaned with detergent, water, acetone, deionized water, followed by isopropanol and dried using compressed dry air. The slides were then spincoated with Accuglass 311 at 3000 rpm for 20 sec., baked at 180 ^{0}C for 60 sec. in air and then cured for 1 hour at 180-425 ^{0}C under nitrogen. The slides were then transferred to a radio frequency glow discharge plasma chamber and treated with 100

watts of RF power under a hydrogen atmosphere (120 torr) for 5 mins in order to modify coating's surface properties (improve wettability)

Polymer resins were spincoated onto the surface of an NLO ormosil film already deposited on ITO covered glass plates. Among the several polymer resins tested, only polyacrylic acid has been found to be a useful protective coating. It is water and alcohol soluble and it could therefore be removed after poling by soaking the sample in a solvent which doesn't affect the quality and integrity of the NLO film.

C.1.4. Preparation of an ORMOSIL containing THS (THSO)

THSO was synthesized using procedures depicted in Figure 4. Trihydroxysulfinate (223 mg, 0.5 mmol) and 3-(triethoxysilyl)propyl isocyanate (371 mg, 1.5 mmol) were mixed with 1 mL chlorobenzene and heated for 24 hours at 110 °C under nitrogen. The chlorobenzene was distilled off and 1 mL isopropanol was added to dissolve the material.
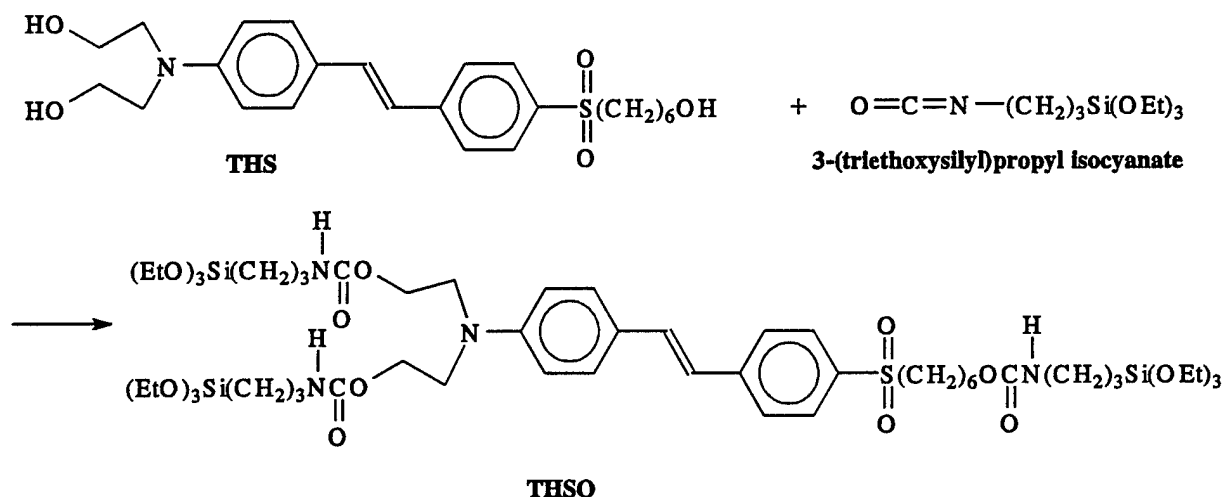

Figure 4 Synthesis of NLO ormosil (THSO) containing THS.

C.2. PREPARATION OF NLO COMPOSITE FILMS

In order to improve the SHG signal stability of DHDO films and to simplify the hydrolysis procedure, the conditions of film formation were systematically changed. In the following description, numeric codes have been used for easy indentification of each composite material.

IV-99-1: To a mixture of DHDO, isopropanol and partially hydrolyzed silica (Si content 1:1) enough water was added for full hydrolysis, *i.e.,* 3 molar equivalent for each $Si(OEt)_3$ and 4 molar equivalent for each $Si(OEt)_4$. The mixture was heated at 60 °C and spincoated. The films were heated for 15 mins. at 100 °C.

IV-99-1

2.4 g DHD-ORM soln. 60 °C   left at room   340 mg H$_2$O   60 °C
+1 g partially   ──────▶   temperature   (Total 3 equiv.)   ─────────
hydrolyzed silica   4 h   for 3 days   ──────────▶   80 mins
                                          340 mg IPA

IV-99-1   100° C   filtered
            ◀──────   & spincoated
(soln. started gelling   15 mins   at 1000 rpm
after ~2 h at r.t.)
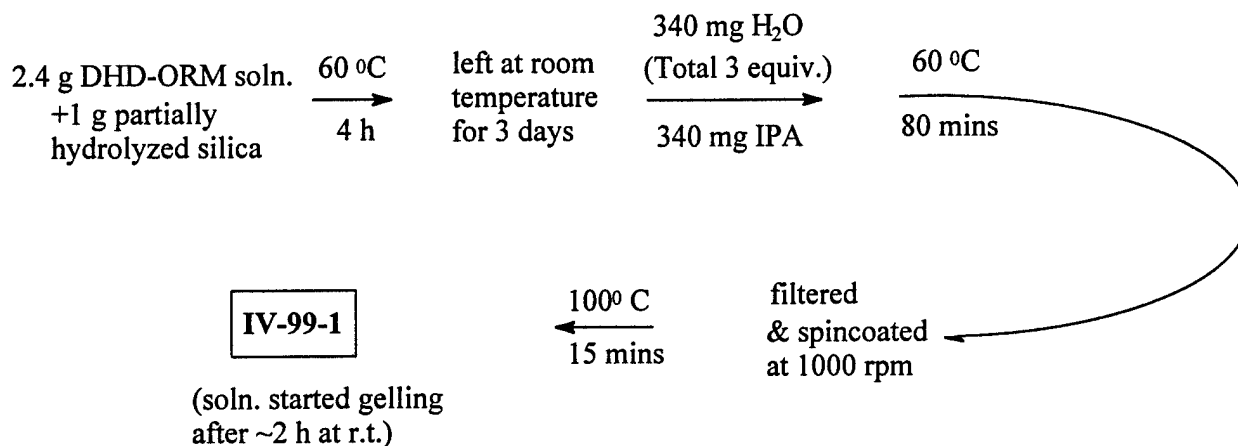
Figure 5 Preparation of IV-99-1 sol-gel composite.

V-3-3: This procedure is the same as IV-99-1, except cyclopentanone and isopropanol were added to prevent gelling. Films were much thinner than IV-99-1.

V-3-3 c

1.2 g DHDO soln.   1. 60 °C / 0.5 h   170 mg H$_2$O   60 °C   2 g Cyclopentanon
+ 0.5 g partially   ─────────────▶   ──────────────▶   ─────────
hydrolyzed silica.   2. 90 °C / 4.5 h   170 mg Isopropanol   80 mins   1 g Isopropanol
                                                        (started gelling)

spincoated at 1000 rpm
V-3-3 c   ◀────────────────   clear but diluted soln

Figure 6 Preparation of V-3-3 sol-gel composite.

V-5-1: Similar to IV-99-1. Films were heated under vacuum at 100 °C for 25 mins.

All the films prepared using the above three procedures did not show any SHG signal at room temperature. The signal increased sharply with temperature, and showed very high values at 180 °C. When the sample was slowly brought back to room temperature, this value dropped to almost zero.

| V-5-1 |

$$1.2 \text{ g DHDO} + 0.5 \text{ g partially hydrolyzed silica} \xrightarrow[3.5 \text{ h}]{60 \ ^{o}C} \xrightarrow[\text{for 3 days}]{\text{left at room temperature}} \xrightarrow[\substack{170 \text{ mg} \\ \text{Isopropanol}}]{170 \text{ mg H}_2\text{O}} \xrightarrow[50 \text{ mins.}]{60 \ ^{o}C}$$
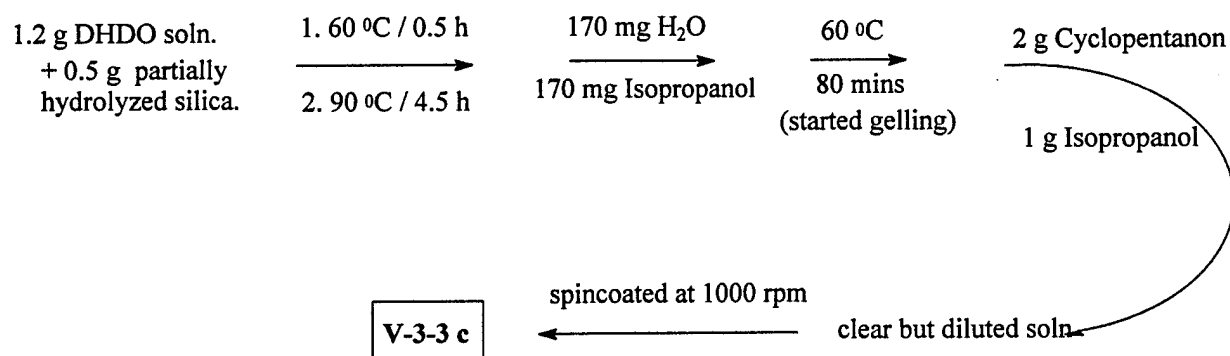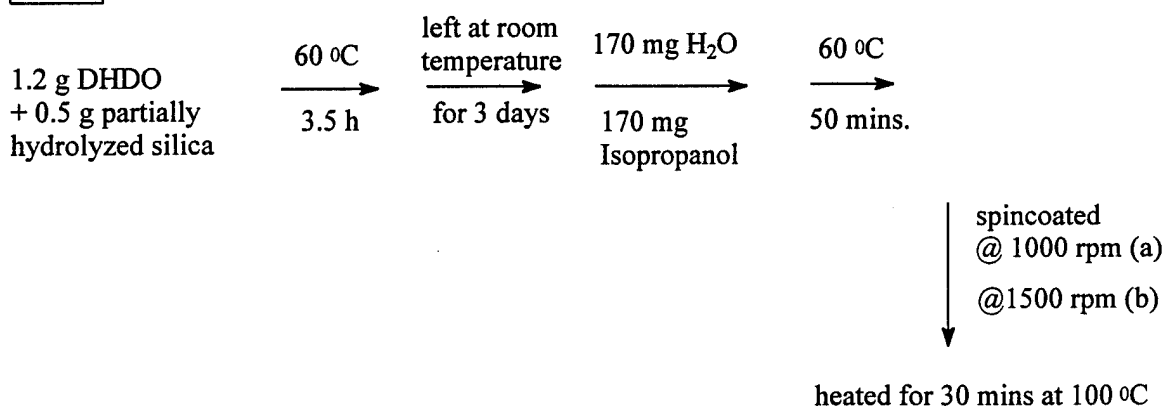
spincoated
@ 1000 rpm (a)

@1500 rpm (b)

heated for 30 mins at 100 °C

similarly prepared mixture + 955 mg Isopropanol $\xrightarrow[\text{@1000 rpm (c)}]{\text{filtered and spincoated}}$ heated 100 °C w/o vacuum then heated under vacuum for 25 mins

Figure 7 Preparation of V-5-1 sol-gel composite

V-10-3b: A 39% aqueous formic acid solution containing 2 molar equivalent water for each triethoxysilane group, was added to DHDO solution in isopropanol. The solution was heated at 60 °C, cooled and mixed with partially hydrolyzed silica followed by addition of butanol and cyclopentanone. The films were spincoated and dried under vacuum at 100 °C for 2.5 h. Film thicknesses were determined to be 0.83 μm.

V-11-2: A 88% aqueous formic acid solution containing 3 molar equivalent water for each triethoxysilane group was added to DHDO solution in isopropanol. The solution was sonicated and heated at 60 °C. The films were spincoated and dried under vacuum at 100 °C for 2.5 h.

Thickness for V-11-2-a : 0.5 μm.
Thickness for V-11-2-b : 0.55 μm.

V-11-2

DHD-ORM (0.5 g)   220 mg formic acid   sonicated for   60 °C
+500 mg IPA   ——————————————→   ——————————————→   ——————————→
                (3 equiv. H_2O / $Si(OEt)_3$)   10 mins at r.t.   30 mins.
                + 500 mg old butanol

filtered and
spincoated
at 1000 rpm

V-11-2   ←——————————   dried in oven
              at 100 °C under vacuum
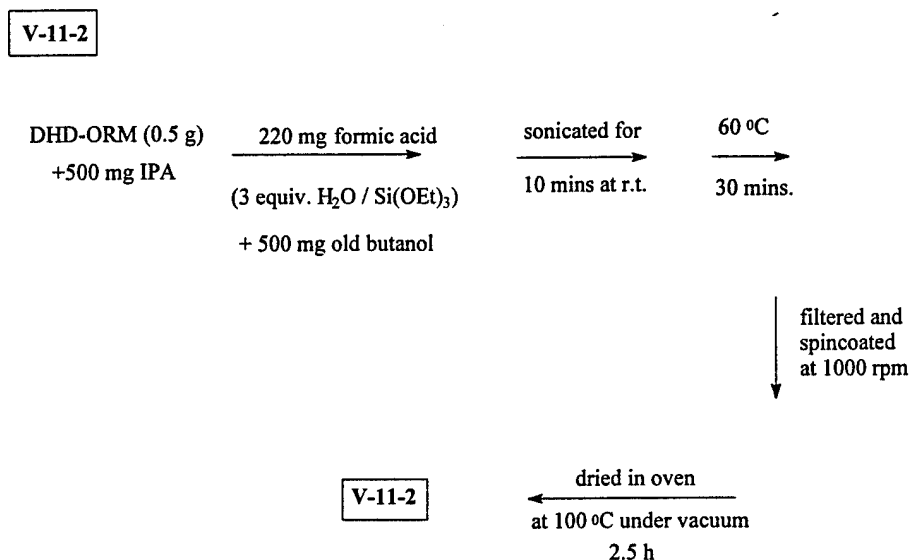   2.5 h

Figure 8 Preparation of V-11-2 sol-gel composite.

V-16-1: A similar procedure as above was followed. Chlorobenzene was present in the system which caused precipitation of ORMOSIL after hydrolysis. Cyclopentanone was added to dissolve the precipitated ORMOSIL.

Thickness for V-16-1-a : 0.3 μm.
Thickness for V-16-1-b : 0.34 μm.

V-16-1

1.04 g DHDO   450 mg formic acid
                     (88%) (54 mg H_2O)
(without removing   ——————————————→   sonicated for 10 mins.
chlorobenzene)**   500 mg butanol   @ r.t.

60 °C
15 mins.

dried at 100 °C   500 mg Cyclopentanone   precipitated out
under vacuum   ←——————————
for 2.5 h.   filtered &
                   spincoated
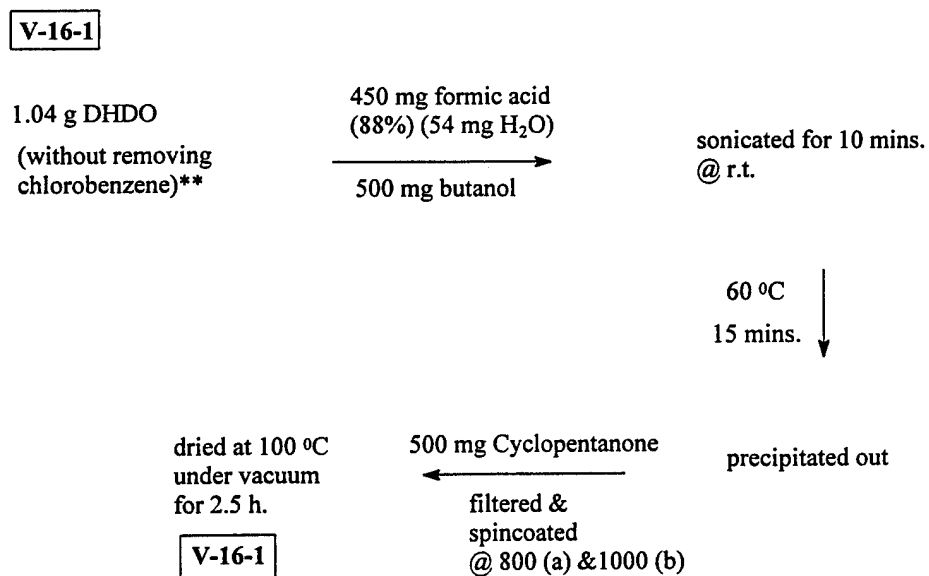V-16-1   @ 800 (a) &1000 (b)

Figure 9 Preparation of V-16-1 sol-gel composite.

V-18-1: Same procedure as V-11-2.

       Thickness for V-18-1-a   : 0.48 μm.
       Thickness for V-18-1b-a   : 0.72 μm.
       Thickness for V-18-1b-b   : 0.71 μm.
       Thickness for V-18-1b-c   : 0.68 μm.

```
           ┌────────┐
           │ V-18-1 │
           └────────┘

                    450 mg formic acid
   DHDO soln.       (88%) (54 mg H₂O)            sonicated for 10 mins.
   in isopropanol  ───────────────────►          @ room temperature
                      500 mg butanol


                                                       60 °C
                                                       5 mins │
                                                              ▼

   dried under vacuum
   for 2.5 h @ 100 °C               spincoated @ 900 rpm
      ┌──────────┐                ◄───────────────────
      │ V-18-1 (b)│
      └──────────┘
```

DHDO soln. in isopropanol $\xrightarrow[\text{500 mg butanol}]{\text{450 mg formic acid (88\%) (54 mg H}_2\text{O)}}$ sonicated for 10 mins. @ room temperature

60 °C 5 mins

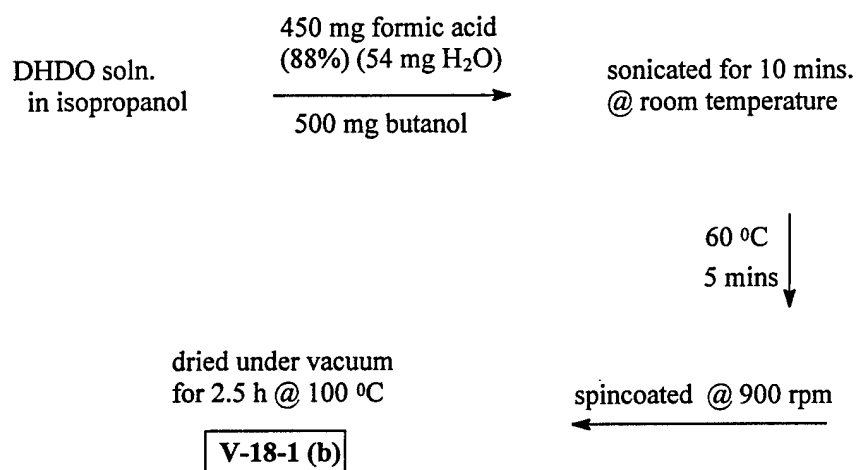dried under vacuum for 2.5 h @ 100 °C

spincoated @ 900 rpm

Figure 10 Preparation of V-18-1 sol-gel composite

V-21-1: The procedure was same as V-11-2. Except that butanol was added just before spincoating the film, to ease the filtration.

       Thickness for V-21-1-b : 0.54 μm.

D.   NLO Properties of the Composites

The electric field poling efficiency depends on a large number of parameters such as the poling temperature, poling electric field, environmental humidity and the material itself. The optimal poling conditions vary from one material to another. For this reason *in situ* poling process has been employed for each sample to determine the best poling conditions. This technique was described in detail in our previous report.

LPT's custom designed experimental arrangement for *in situ* poling studies has been modified by placing a thin sapphire window between the heating plate and the samples in order to achieve uniform sample temperature. Sapphire was selectedas the window material because of its good thermal conductivity.

It has already been emphasized that during our research on the efficiency of electric field poling it has been established that the majority of materials suffer surface damage because of the exposure to high kinetic energy ions during the corona discharge. Our first attempts aimed at reducing this problem used thin layers of several organic dielectrics such as photocurable epoxy resins (e.g., Norland), other polymers (polyacrylic acid) or even Spin-on-Glass silicate polymer (Accuglass 311, DuPont). This approach, however, reduces the effective electric field applied to a sample and, as a result, yields samples with low nonlinearity. In addition, most materials used as protective layers were difficult to remove. A notable exception was polyacrylic acid which is a water soluble polymer and could be removed by soaking the poled sample in deionized water for about 30 minutes. However, this particular polymer was found to be unsuitable for ormosil composites because it had tendency to react with ormosils under strong electric field at elevated temperatures (above 140 $^{\circ}$C).

These observation led us to design a different poling apparatus to be used on materials which have already been established by *in situ* poling technique. Figure 11 illustrates this design. The main improvement is the introduction of a mesh (set of thin wires) between the corona discharge filament and a sample's surface. A potential of the same polarity as the discharge bias, but much lower in magnitude is applied to the mesh which, thus, acts to slow ionized species (ions). Through the adjustment of bias voltage applied to the screen relative to that needed for corona discharge, an efficient control of the ions' kinetic energy can be achieved without compromising the strength of the poling field across the sample. In this manner, serious surface damage resuting from the bombardment of the sample surface by highly accelerated ions can be prevented. In addition, the apparatus has been designed to pole samples under dry atmosphere of different gases such as nitrogen, argon, helium, etc. This feature provides additional control over poling conditions (known ionic species) and a means to avoid highly reactive and oxidizing ions which can easily damage sample.

All *in situ* experiments were carried out with a Q-switched Nd:YAG laser operating at 10 Hz with a fundamental wavelength of 1.064 μm. A p-polarized fundamental beam was used for

all the second-harmonic generation *in situ* measurements. All NLO films were spin coated onto Indium Tin Oxide (ITO) covered glass substrates. The second-harmonic light generated from the sample passes through a series of filters and is detected by a boxcar signal analyzer.
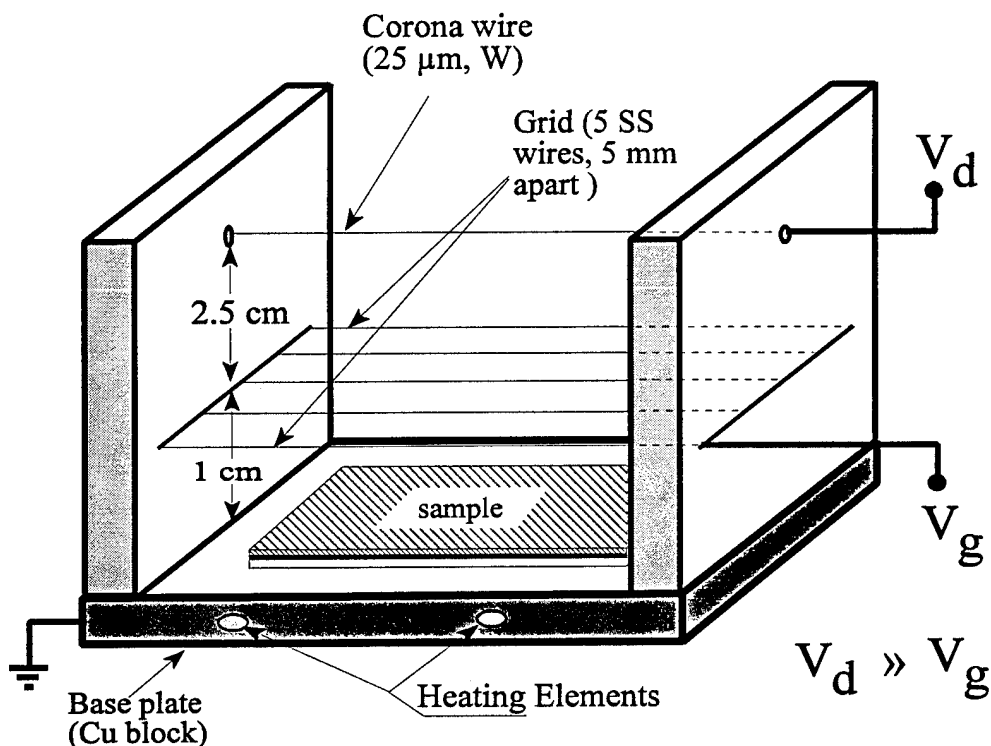
Figure 11 Electric field poling apparatus employing metal grid.

D.1.   POLING CHARACTERISTICS AND TEMPORAL STABILITY

The *in situ* SHG experiments were conducted on all of the material composites described in this report; the ones showing the greatest promise are pure DHDO and DHDO/SiO$_2$ composite films. The *in situ* technique provides real-time information about the matrix and its ability to retain the chromophores in their preferred orientation.   This property can change dramatically as the materials are thermally processed. In both composites, the second-order chromophores were shown to be electrically aligned at room temperature. For DHDO composites, the second-harmonic signal (monitored as a function of heat treatment with the field applied) typically shows an increase with temperature and reaches a maximum at 135 ^{0}C. Any further temperature increase results in substanial decay of the SHG signal. Upon cooling to room temperature, only about 75% of the SHG signal was usually retained. Measurements of

temporal stability of the induced alingment revealed that this type of poling was not effective. The SHG signal dropped in one month to a level of about 40% of that immediately after the poling. Since such stability is not acceptable for any practical application we have desinged another poling strategy which was more effective for sol-gel and ormosil based composites.

In place of a commonly used temperature "ramp" strategy as presented above, we used a slow ramp/soak approach. This poling scheme involves slow temperature increase to a set point about 30 degrees higher than the preceding one and holding the sample at that temperature for 1 to 2 hours. The hold time at the highest temperature (in majority cases it was 135 °C to 145 °C) was usually 3 hours. Longer curing times up to 12 hours as well as higher temperatures were also attempted, but resulted in partial degradation of the composite material

Employing ramp/soak poling and curing with NLO ormosil based composite films improved poling efficiency and stability of the induced noncenrosymmetric structures. Figure 12 schematically depicts temperature ramp/cure scheme. In general, the second
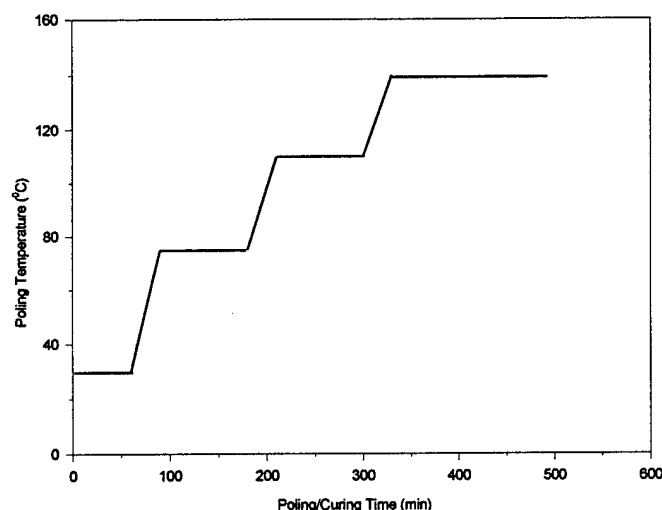

Figure 12 Electic field poling profile used for sol gel ormosil NLO composites

harmonic signal followed this ramp schedule for the majority of samples, i.e., there was a significant increase of SH intensity with every increase of the sample's temperature which, then, would level-off during the soak period.

The length of dwell times was determined experimentally and was different for each cure temperature. For example, at temperatures below 100°C, hold/cure times were in general shorter than those above 100°C. It was found that, at low temperatures, the time needed to reach a plateau of SHG signal was shorter than at high temperatures. This could be related to the proximity to the glass transition tempearture, T_g, and the sample conductivity.

Sol-gel composite materials can be viewed as thermosetting resins, i.e., their molecular weight and, concomitantly, T_g increases as the numbert of crosslinked sol-gel molecules becomes larger. The increase of ionic conductivity in many amorphous polymers at temperatures above the glass transition temperature (wherein phase transformation from a glassy to a rubbery state takes place) is comonly explained by an increase of the material's free volume.[5] Above T_g the free volume becomes redistributed more uniformly because of a greater flexibility among the polymeric chains. Since the mechanism of ionic conductivity is diffusion through vacancies, ionic diffusion (conductivity) can occur over long distances (long range conductivity). In contrast, at temperatures below T_g, the vacancies do not form continous paths and, consequently, diffusion of ions (conductivity) is limited. Such dependence has been observed for PMMA and other polymers,[6] including sol-gel composites.[7]

The observed improvement in poling efficiency on our composite materials by using a slow ramp/soak method can be explained by increased degree of crosslinking between ormosil and silica chains which, effectively, results in increase of the material's T_g. Thus, each long cure period increases the T_g value, reduces ionic conductivity and increases the electric field strength across the sample. After several ramp/soak steps at higher temperatures further crosslinking and poling becomes more difficult because the matrix is already very stiff. Thus, much longer hold times are needed to reach equilibrium SHG.

The second-order susceptibilities of the material composites presented in this report have been measured using the angular dependence method. The results have been obtained by comparing the SHG intensity from the materials to that from a Y-cut quartz crystal. The thickness of the films is measured using a Tencor® Alpha Step 100 profilometer. These data are listed in Table I along with the molar fraction of the NLO chromophores in sol-gel/ormosil composites and

Table I Molar fraction of chromophore, $\chi^{(2)}$ values of the poled sol-gel ormosil composites composites and chrompophore properties.

NLO Chromophore	Molar fraction in sol-gel composite	$\chi^{(2)}$ (10^{-7} esu)	λ_{MAX} (nm)	Chromoph. dec. temp. (°C)
DHD	0.4	4.7	435	285
NPP	0.3	2.6	393	310
THS	0.2	0.1	383	267

other chromophore parameters. Decomposition temperature and UV-VIS spectra of the chromophores were recorded on a Shimatzu Differential Calorimeter and UV-VIS Spectrometer, respectively.

The temporal stability of the poled structures at ambient conditions have been monitored for an extended period of time by repeatedly measuring the SHG intensity. As can be seen from Figure 13, these composites show, at room temperature, remarkable stability of the field induced alignment weeks after the poling field has been removed.

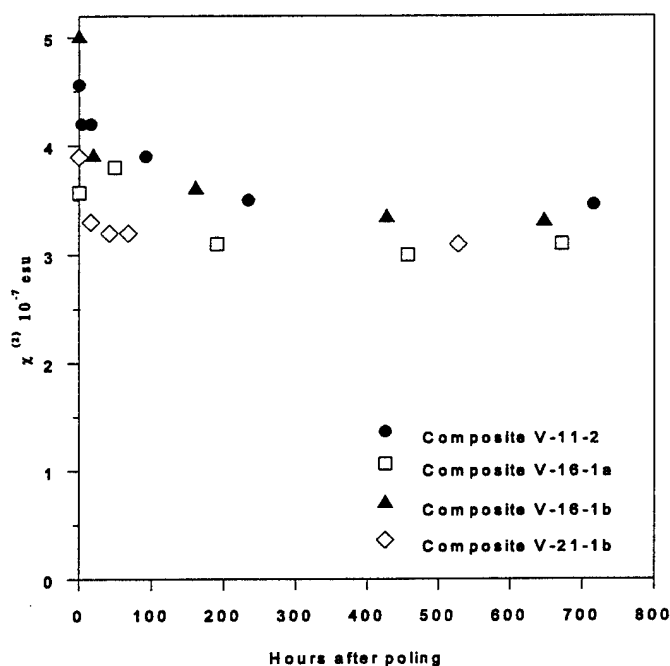Temporal stability of $\chi^{(2)}$ for selected-sol gel/ormosil composites

Composite V-11-2
Composite V-16-1a
Composite V-16-1b
Composite V-21-1b

Hours after poling

Figure 13　Temporal stability of $\chi^{(2)}$ coefficient for selected sol gel composites of DHDO ormosil.

D.2. THERMAL STABILITY

The thermal stability of poled structures was tested dynamically and isothermally. Figure 14 depicts the dynamic thermal stability for two poled ormosil composites, V-16-1 and V-38-2.
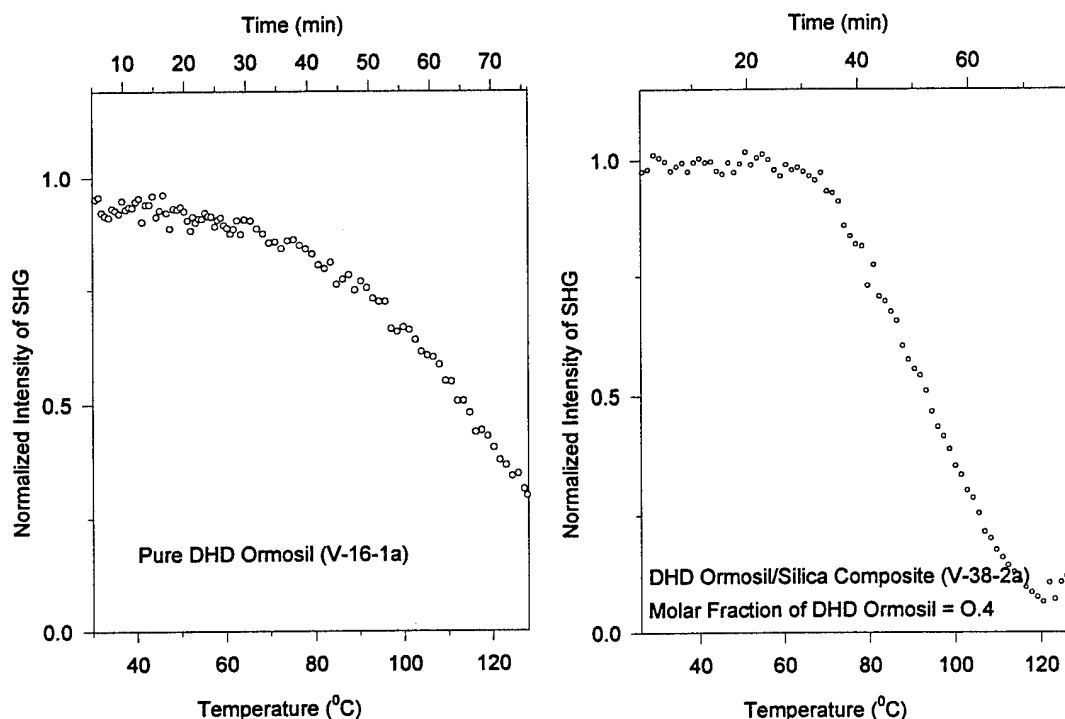

Figure 14 Dynamic thermal stability of $\chi^{(2)}$ coefficient for poled sol gel/ormosil composite films containing DHD chromophore.

The stability of the poled structures shown in Figure 14 can be correlated to the molecular structure of the polymers. The rapid decrease of SHG signal at around 70°C for DHDO/SiO$_2$ composites indicates a low degree of crosslinking and a rather low glass transition temperature. Indeed, a DSC scan revealed an obvious transition around 70°C. This composite was poled under continous thermal ramping with a single cure time of 2 hrs at 135°C. Such a short time may not be sufficient for the composite material to undergo extensive crosslinking to provide a rigid matrix for poled chromophores, as was discussed above.

Dynamic thermal stability for pure ormosil composites show somewhat different behavior. The composite was poled using a ramp/soak schedule containing a soak of 3 hrs at the highest temperature (135⁰C). The total time of the poling process was about 10 hrs. The decrease of SHG signal does occur over broader range of temperatures. This feature indicates that more extensive crosslinking between polymer chains took place during poling process. It has to be emphasised that the ormosil requires longer times to form highly crosslinked matrix structure because of lower reactivity of trialkoxysilanes towards hydrolysis as compared to tetraalkoxy silanes. This issue was discussed in detail in our previous annual report.

E.   Wave guide Properties of Sol-Gel Materials

One of the primary goals of this Phase II development effort was to fabricate low optical loss second order NLO wave guides using sol-gel processed inorganic/organic composites. We have already disscused that sol-gel materials, being primarily composed of SiO_2, can be made into good optical quality devices. The approach throughout this task was to use ormosil composites in order to increase the materials' homogeneity as well as the number density (in this case the molar fraction) of NLO chromophores. It is clear that in doped systems the number density of the chromophore is limited because of the inevitable phase segregation and, consequently, loss of the optical quality. The best known host matrices such as polycarbonates can accomodate up to 60 wt% of guest molecules. However, there are only certain types of dopant species compatible with these polymers which can be doped to such high levels. Unfortunately, high β value chromophores neither belong to these classes, nor are they higly soluble in solvents suitable for polymeric matrices. An additional shortcoming of polycarbonates is their low glass transition temperature.

In this task, the staff of LPT focused its work on optimizing several processing conditions in an effort to fabricate films of good optical quality and with controlled thickness. Secondly, the electric field poling process was carefully studied in order to establish conditions which would minimize damage to NLO guiding layers. These efforts were necessary since the material requirements for optical processes in a guided wave geometry are very stringent (see Table II below).

Table II   List of typical requirements for optical wave guide materials

Material Requirements for Nonlinear Wave Guide

1.   Control of refractive index
2.   Control of thickness
3.   High optical quality
4.   Other material requirements
    (a) high mechanical strength so the wave guide is not easily damaged
    (b) excellent environmental stability
    (c) high optical damage threshold
    (d) the ease with which the material can be cost effectively incorporated into an integrated optical format

E.1. WAVEGUIDING CHARACTERISTICS IN SOL-GEL DERIVED DHD ORMOSIL COMPOSITE FILMS

The experiments establishing wave guiding quality of ormosil based sol-gel films were tested by coupling radiation from an Ar^+ laser pumped tunable Ti-Sapphire laser with the help of $SrTiO_3$ prism coupler. The ormosil films were spun coated on 2 × 1 inch fused silica slides and overcoated with spinnable glass (Accuglass 311, DuPont) which served as a low index of refraction buffer layer. Several laser wavelengths between 750 nm to 830 nm were used in the experiment. Refractive indices of the composite films varied according to differences in their composition; for example, pure DHDO films had the highest n values which continously decreased as the content of SiO_2 increased.

The total waveguide losses were measured by recording scattered radiation from a coupled wave guide mode. A CCD camera was used to determine changes in the intensity of scattered light along the propagation direction. Typical results for pure DHDO films are shown in Figures 15 to 17 which display both the measured changes in light intensity and the calculated propagation losses as a function of propagation distance for TE and TM modes at three different wavelengths.

The results show that propagation losses are smaller for longer wavelngths. This trend is expected since the major loss mechanisms at low intensity levels (scattering and linear absorption) are wavelength dependent. Scattering loss scales approximately as λ^{-2} (Rayleigh scattering)[8] and linear absorption follows standard Lambert-Beer law. Thus, for wavelengths further away from electronic transitions, absorption losses become smaller because of a smaller extinction coefficient. A similar trend was observed for the sol-gel composites containing $NPP/SiO_2/TiO_2$, as reported in our previous annual report. Optical losses in current waveguides are in a range of 1.6 to 4 $dBcm^{-1}$ (see Figure 18) and are higher than those for NPP composites. However, we expect that with improved processing parameters and fabrication conditions (clean room) propagation losses can be lowered to less than 1 $dBcm^{-1}$ at 800 nm.

Another advantage of DHDO waveguide films is that the content of unreacted hydroxyl groups can potentially be made smaller than in silica sol gel based doped systems because a molecule of ormosil contains one less alkoxy group. It had been determined by our previous studies and reported a year ago that the presence of hydroxyl groups in the sol-gel matrix is responsible for increased absorption losses at around 1.3 μm. This is because the first overtone vibrations of the O-H group are at 3657 cm^{-1} or 1367 nm (symmetric stretch) and at 3756 cm^{-1} or 1330 nm (asymmetric stretch).

The results presented above clearly indicate that optical quality wave guides can be prepared from ormosil/sol-gel materials and composites containing NLO chromophores. The process of preparing these wave guides is definitely amenable to integrated optical devices. The optical losses in these materials are already acceptably low for practical applications and are expected
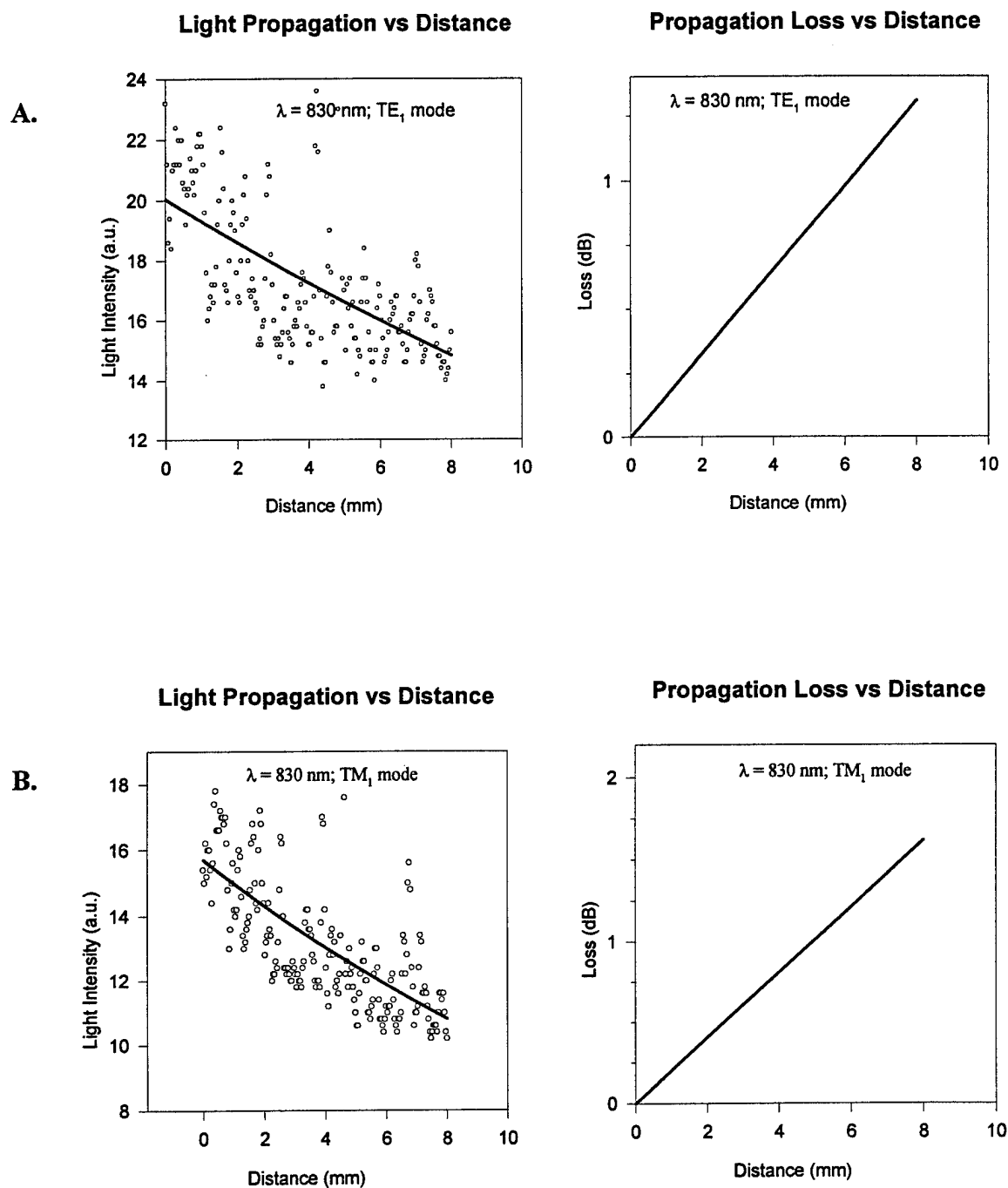
Light Propagation vs Distance   **Propagation Loss vs Distance**

A.

Light Propagation vs Distance   **Propagation Loss vs Distance**

B.

Figure 15   Variation of scattered light intensity and waveguide propagation losses for TE
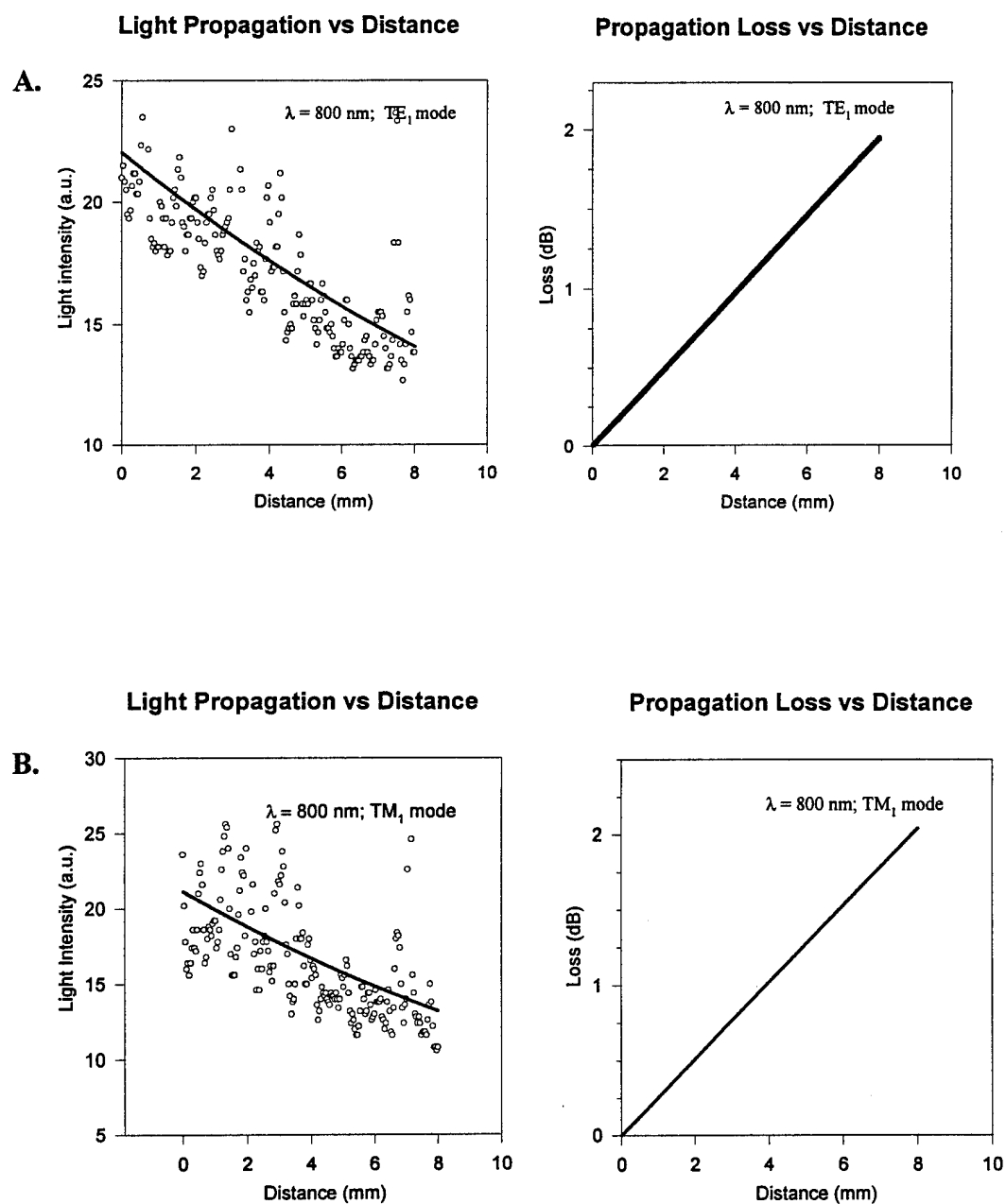(**A**) and TM (**B**) modes at 830 nm for pure DHD ormosil film.

Light Propagation vs Distance

A.

Propagation Loss vs Distance

Light Propagation vs Distance

B.

Propagation Loss vs Distance

Figure 16   Variation of scattered light intensity and waveguide propagation losses for TE (**A**) and TM (**B**) modes at 800 nm for pure DHD ormosil film.
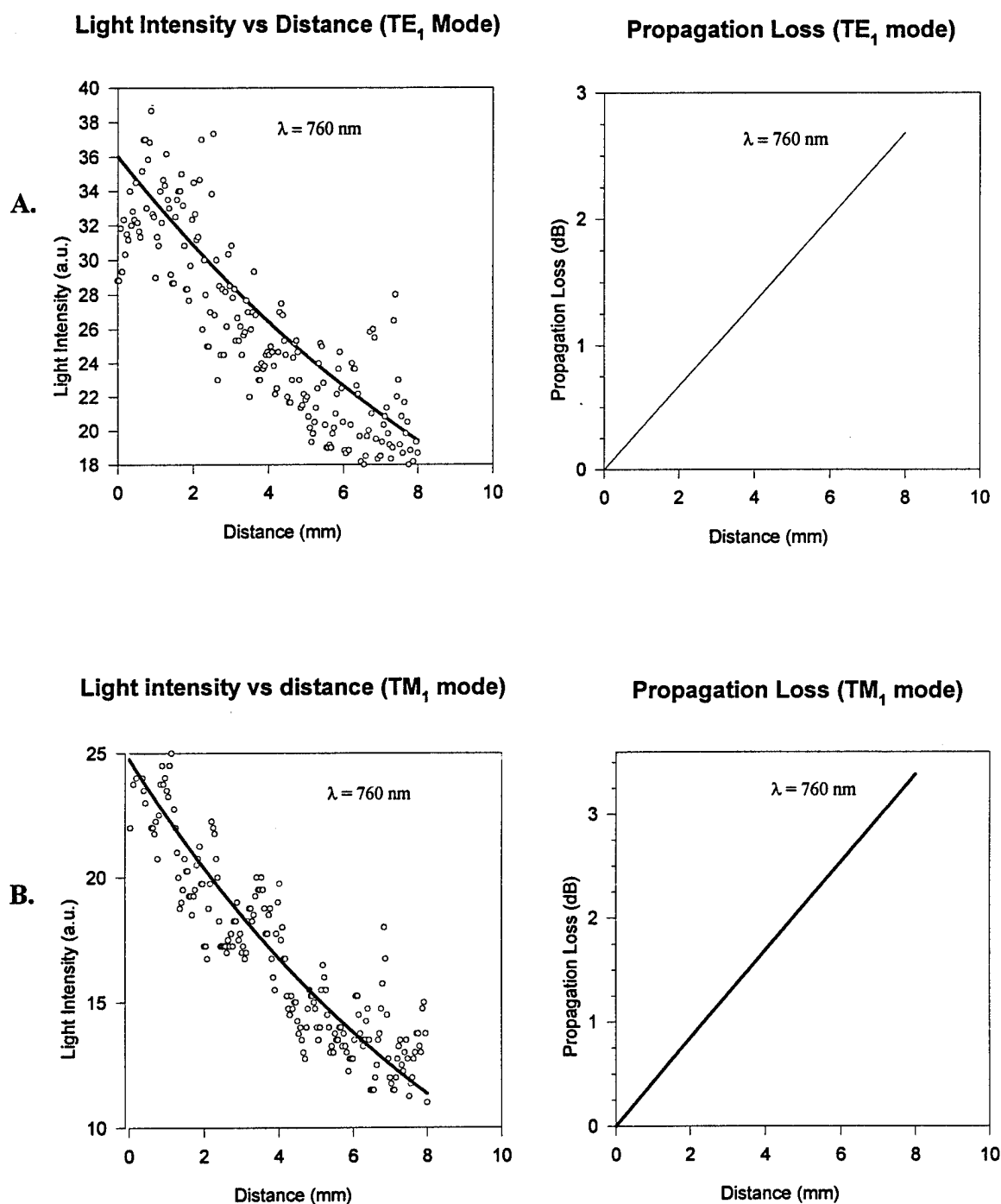
Light Intensity vs Distance (TE$_1$ Mode)

A.

$\lambda = 760$ nm

Propagation Loss (TE$_1$ mode)

$\lambda = 760$ nm

Light intensity vs distance (TM$_1$ mode)

B.

$\lambda = 760$ nm

Propagation Loss (TM$_1$ mode)

$\lambda = 760$ nm

Figure 17   Variation of scattered light intensity and waveguide propagation losses for TE (**A**) and TM (**B**) modes at 760 nm for pure DHD ormosil film.

to be substantially improved. This fact, coupled with the flexibility of the sol-gel process (variable index of refraction, chromophore concentration and replacement, etc.) provides sufficient reason to believe that enhanced materials can be prepared for second-order NLO applications.
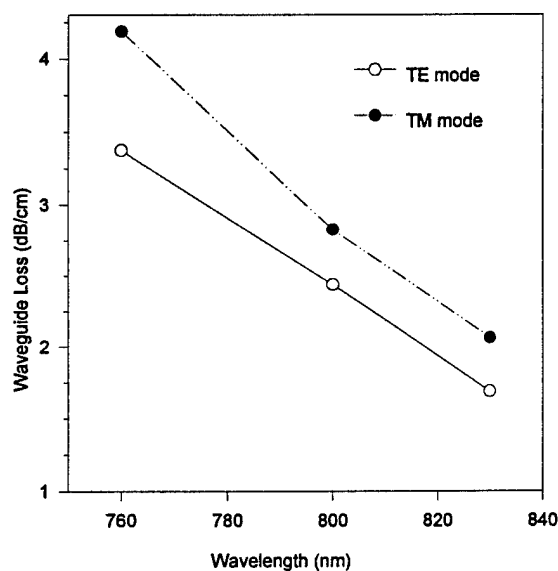

Figure 18   Dispersion of wave guide propagation loss in DHDO composite films for TE and TM modes.

PLANNED WORK

There are several requirements imposed on a $\chi^{(2)}$ material; four of them are imperative if it is to be effective in practical devices. These are:

(1) large $\chi^{(2)}$ value
(2) optical transparency
(3) ease of processing into a desired form
(4) temporal and thermal stability of the second order responses*

(*) A proposed military standard for thermal stability of second-order NLO property is 100% retention of NLO activity after 1000 hrs at 100 °C or 30 minutes at 300 °C; LPT is working to develop materials that can meet this high temperatures requireements.

Sol-gel materials have been demonstrated to be effective electrooptical materials. The strength of the second order response, the ability of the matrix to retain the noncentrosymmetric alignment and the low losses obtained from wave guides are all necessary achievements if these materials are to be used in commercial integrated electrooptical devices.

There are several organic materials that are being developed in a large number of research groups; these efforts, being conducted for the last several years, are driven by the fact that organic materials have high optical nonlinearities and can be more readily processed. However, during past year appreciable progress in thermally stable NLO chromophores and poled polymeric structures has been made.[9,10] For example, 100% retention of electrooptic coefficient as large as 16 pm/V after 1000 hrs at 90°C has been reported.[9]

The materials discussed in this report meet many of the above requirements for effective electrooptical devices: they are tractable and exhibit large and stable $\chi^{(2)}$ values. Our continued efforts will be directed at:

(1) improvement on the thermal stability of the composites and
(2) assessing the full potential of these materials for commercial applications.

For any practical device, one may expect that the environmental conditions (e.g., temperature) may not necessarily be kept constant over a long period of time or during the device fabrication process. Thus, a major concern, to be more fully addressed, is whether these materials will maintain the noncentrosymmetric alignment at elevated temperatures (100°C or more) over an extended time period (more than 1000 hrs).

The staff of LPT is placing the emphasis on $\chi^{(2)}$ ormosils. This approach enables higher concentration of chromophore to be placed in the composites without introducing phase separation and the concomitant loss of optical quality. The proper selection and incorporation

of ormosils and additional polymers that can be crosslinked will enable the chromophores alignment to be retained at higher temperatures.

It has been shown that the chromophores exhibit a decrease in their β value at elevated temperatures below their decomposition, and that this is likely due to reactions with oxygen. The NLO ormosils developed at LPT contain chromophores which show high decomposition temperatures. Thus, it is expected that their β values will be highly stable. This phenomenon will be further evaluated. In addition, since the materials are ordinarily covered with buffer layers when they are used in a device, it may not be a significant problem since the buffer does offer some protection.

The development of these materials into useful devices requires that these materials can indeed modulate at high frequencies and with sufficient amplitude. These tasks will require the use of a wave guide geometry. Many of the proposed materials have already been fabricated as wave guides and found to have very low optical losses. The best materials will be selected and tested for high frequency electrooptic modulation using a wave guide device.

LPT is currently presenting the results obtained thus far in conferences and directly to companies that are perceived to be commercial Phase III partners. These efforts will be increased as the answers to critical questions are ascertained.

References

1. Puccetti, G.; Perigaud, A.; Badan, J.; Ledoux, I.; Zyss, J., (1993) *J. Opt. Soc. Am.*, **B10**, 733 and references therein.
2. Girton, D. G.; Kwiatkowski, S. L.; Lipscomb, G. M.; Lytel, R. S., (1991) *Appl. Phys. Lett.*, 58, 1730.
3. Teng, C. C., (1992) *Appl. Phys. Lett.*, **60**, 1538.
4. Ferm, P. M.; Knapp, P. W.; Wu, C.; Yardley, J. T.; Hu, B. B.; Zhang, X. C.; Auston, D. H., (1991) *Appl. Phys. Lett.*, **59**, 2651.
5. T. Miyamoto, K. Shibayama, *J. Appl. Phys.*, **44**, 5372 (1973).
6. J. Owen, in "Polymer Properties", C. Booth, C. Price, Eds., *Comprehensive Polymer Science*, **vol. 2**, Pergamon Press, 1989, pp. 669.
7. S. Kalluri, W.H. Steier, Z. Yang, C. Xu, B. Wu, L.R. Dalton, Y. Shi, J.H. Bechtel, *SPIE Proceedings*, **vol. 2285**, 67 (1994).
8. P.K. Tien, *Appl. Opt.*, **10**, 2395 (1971).
9. A.K-Y. Jen, K.J. Drost, Y. Cai, V.P. Rao, L.R. Dalton, *J. Chem. Soc., Chem. Commun,*965(1994); A. K-Y. Jen, K.J. Drost, Y. Cai, V.P. Rao, L.R. Dalton, *J. Chem. Soc., Chem. Commun,* 2711 (1994).
10. A.K-Y. Jen, V.P. Rao, K.J. Drost, K.Y. Wong, M.P. Cava, *J. Chem. Soc., Chem. Commun,* 2057 (1994); A.K-Y. Jen, K.Y. Wong, V.P. Rao, K.J. Drost, Y.M. Cai, *J. Electr. Mater.,* **23**, 653 (1994); V.P. Rao, K.Y. Wong, A.K-Y. Jen, K.J. Drost *Chem. Mater.,***6**, 2210 (1994).